

Thermodynamic Modelling of Directed Melt Oxidation Processing for Ceramic Matrix Composites

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Abstract

Equilibrium thermodynamic modelling is used to predict the likely species that will form in the production of ceramic matrix composites using Li, Mg, Na and Zn as external dopants, with growth into an alumina preform. The modelling indicates strong similarities between all these systems. Interpretation of the results suggests that initiator dopants for the directed melt oxidation of aluminium should be volatile at the reaction temperature and should be capable of forming a mixed oxide phase with aluminium. © 1999 Published by Elsevier Science Limited. All rights reserved

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1 Introduction

Directed melt oxidation is a relatively low temperature route for the production of ceramic matrix composites. Directed melt oxidation involves the growth of a ceramic reaction product by the directed oxidation of a bulk molten metal by a gas. The product may contain several percent of residual metal and reinforcements may be readily incorporated in the product by growing the reaction product through a preform comprised of ceramic particles, platelets and fibres. Dopants are required to initiate and maintain the growth process and it is this feature which distinguishes the DMOX process from other reaction bonding processes. Growth is limited by the presence of inert (barrier) powders which may be used to define the shape of the desired product.

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The dopants may be incorporated into the reaction system in a number of different fashions. The original patents and much of the published work in this area concentrate on the use of 'internal' dopants whereby the dopants are introduced via specially prepared aluminium alloys.^{1,2} However dopants may also be introduced 'externally'.³ In this case, for growth into free space, the dopants may be placed adjacent to the metal reservoir (Fig. 1; case I), whereas for production of a composite the dopants may be mixed with a preform body (see Fig. 1; case II). External dopants can be introduced in elemental or compound form. Composite growth has been demonstrated in the aluminium/alumina system using Li, Mg, Na and Zn as external dopants.^{3–6} Mg and Zn were introduced in elemental form,^{3,6} Li as lithium carbonate and Na as beta alumina.^{4,5} Both composite growth into free space (case I) and composite growth into a preform (case II) have been studied but for the purpose of this paper attention is concentrated on growth into a preform. The preform consisted of either 1.23 wt% lithium carbonate (equivalent to 0.5 wt% Li_2O) mixed with particulate alumina, 5 wt% magnesium and alumina, tabular alumina containing β -alumina (sodium aluminate) sufficient to give a concentration of 0.36 wt% Na_2O , or 2.5 wt% zinc and alumina. These quantities correspond to 0.24 at% Li, 0.17 at% Na, 1.45 at% Mg and 0.75 at% Zn in the final composite.

Although directed melt oxidation is not an equilibrium process Guillard *et al.*⁶ have shown that it is possible to make useful predictions about likely phase formation during directed melt oxidation by modelling the reaction system with equilibrium thermodynamics. Guillard *et al.* concentrated on a reaction system that contained both Mg and Si as dopants. This paper reports the results of equilibrium thermodynamic calculations on simpler aluminium/alumina systems that contain a single dopant: Li, Mg, Na or Zn introduced externally.

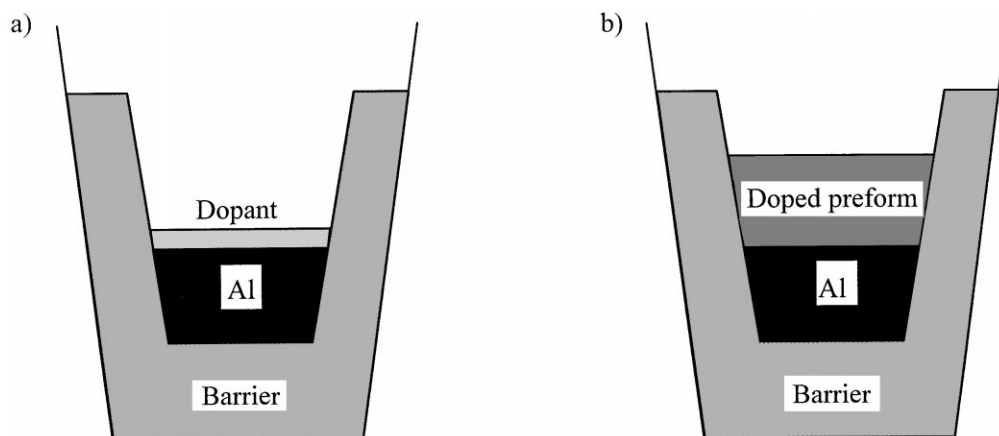


Fig. 1. Sample set-up for growth into (a) free space (case I) or (b) a preform body (case II).

The results for all four dopants are compared to experimental results previously reported^{3–5} or recently obtained and common features are highlighted.

2 Thermodynamic Modelling

Equilibrium thermodynamic calculations were carried out using MTDATA⁷ and FACT.⁸ For the dopants Mg and Li the thermodynamic data were complete and covered the properties of the liquid and solid alloys as well as the possible solid compounds and gases. MTDATA was used to model the Mg and Li doped systems with data taken from SGTE (Scientific Group Thermodata Europe) databases, SGSOL and SGSUB. For the Li doped system the Al-Li data was taken from Ansara⁹ and for LiAl_5O_8 from Byker *et al.*¹⁰ The terminal solid solutions and the liquid solutions for Al-Li, Al-Mg, and Al-Zn were modelled with Redlich-Kister polynomials to deal with the interactions. Al_2Li_3 and Al_4Li_9 together with β , ϵ and ζ Al-Mg phases were treated as stoichiometric compounds and the non-stoichiometric AlLi and $\text{Al}_{12}\text{Mg}_{17}$ phases were treated with a sub-lattice model. In the case of the Na-doped system thermodynamic data for the Al-Na alloys were sparse and only the dilute solutions in aluminium were modelled with the activity coefficient of Na taken from Fray¹¹ and assumed constant at 300, the data for $\text{NaAl}_{11}\text{O}_{17}$ was from Gros *et al.*¹² and for $\text{NaAl}_9\text{O}_{14}$ and $\text{Na}_2\text{Al}_{12}\text{O}_{19}$ from Eriksson *et al.*¹³ FACT was utilised for the calculations in the Na doped system and the FACT database provided full thermodynamic information on the relevant solid compounds and gaseous species not covered by references.^{11–13}

Some difficulty was experienced with modelling the use of lithium carbonate as a dopant. The data provided by FACT and MTDATA differed significantly and gave a difference of ca 300 K in the predicted thermal decomposition temperatures. In

addition, using MTDATA convergence of the calculations was not achieved in region 1. For the purposes of this paper we present the results of a calculation made using Li_2O as the dopant and comment that in region 2 the use of lithium carbonate in the calculations had no significant effect on the amounts of spinel, aluminium nitride, alumina or nitrogen, but dropped the predicted vapour pressure of Li by a factor of 19.9 with consequent changes in partial pressures of Li species containing oxygen, as the predicted partial pressure of oxygen was virtually unchanged. Small quantities of $\text{CO} < \text{g} >$ and $\text{CO}_2 < \text{g} >$ were predicted for systems where carbonates were used and in cases where sodium carbonate was considered this could also lead to small quantities of $\text{NaCN} < \text{g} >$ when no preform was used.

In the experimental directed melt oxidation systems, composites were produced using nominally 50 g blocks of Al. This is equivalent to 1.8532 moles of Al and this quantity was assumed in the thermodynamic modelling. The reactions were carried out in air and a $\text{N}_2:\text{O}_2$ ratio of 79:21 was assumed in the model. The calculations were performed for each composite at atmospheric pressure and a fixed temperature, in an attempt to simulate the real conditions throughout a composite. During directed melt oxidation there will be an excess of oxygen at the free surface whereas near the metal surface there will be a limited oxygen supply, combined with efficient gettering by the metallic components, so the oxygen potential near the metal surface should be low. Thus there is an oxygen variation through the system starting at a very low level at the surface of metal reservoir (set at 1×10^{-5} moles) and increasing to an assumed excess of 10% over that required to completely oxidise the metallic components at the free surface.

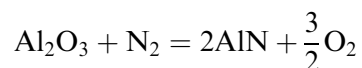
The reaction also involves changes in the amount of the other reactants including nitrogen, dopants and elements contained in the preform. For the

purposes of this model we assume a linear change in the amount of the reactants as the oxidation front moves through the charge and use the parameter α to step the amount of the reactants from that ruling at the surface of the metal reservoir 'lopox' to the free surface 'hipox' in 100 steps. The scale associated with the abscissa shows values of α and represents the progress of the total oxidation reaction. The limitations of the model are obvious in terms of the neglect of movement of gaseous species through the pores in response to pressure and activity gradients.

The system is assumed to be isothermal although heat is undoubtedly released during oxidation. Under adiabatic conditions the heat released in the middle of the preform containing beta alumina could lead to a temperature of ca 3500 K. However, the authors consider that the slowness of the oxidation process makes it possible, as a first approximation, to treat the reaction as isothermal. It is recognised that the details of the oxygen, dopant and thermal profiles are likely to be complex but they are difficult to predict without information on the kinetics of the rate controlling reactions. The approach used in this paper appears to be the simplest way possible of drawing attention to the way in which the oxygen potential can affect vapour phase transport of the dopants and influence differently the formation of the compounds formed between alumina and the oxides of the dopants.

The results for all of the dopants show three regions. Region 1 corresponds to the fraction α reacted $0.0 < \alpha < 0.15$; region 2 to $0.15 < \alpha < 0.90$ and region 3 to $0.90 < \alpha < 1.00$ (all these values are approximate). In region 1 the high volatility and activity coefficient of the dopant Na at 1453 K means that it can generate virtually the entire pressure of 1 atmosphere which was assumed in the conditions for the calculation. For zinc it can only generate this pressure when about 12% of the total zinc has been added and lithium and magnesium are never able to generate a partial pressure of 1 atm. In the absence of volatile species capable of generating 1 atm pressure required by the model no gas phase is produced in region 1, the Li, Mg and Zn remaining in the liquid aluminium alloy and the nitrogen and oxygen forming aluminium nitride and alumina. In the case of sodium the oxygen partial pressure is very low in region 1 associated with the presence of liquid aluminium alloy. Across the region there is a decreasing concentration of liquid aluminium and an increasing concentration of AlN. Figures 2(a)–5(a) show the amount of the various species formed for each of the dopants—Mg, Li, Na and Zn.

For region 2 of all of the diagrams—aluminium nitride and alumina coexist and the oxygen potential is controlled by



As the nitrogen pressure rapidly approaches 1 atm this means that the oxygen potential is virtually constant and this together with the presence of alumina, means that the aluminium partial pressure is also virtually constant in region 2. The magnitude of the oxygen partial pressure is sufficient for the lithium and magnesium spinels to form but not for β -alumina or the zinc spinel to form. The low value of the partial pressure of aluminium in this region means that the only reactants easily transported through it are the dopants. As oxidation and infiltration of the preform proceeds through region 2, increasing amounts of zinc or sodium are added to the system and all of it enters the gas phase. Their partial pressures fall through region 2 as the volume of the gas phase increases through nitrogen entering the gas phase with the total pressure fixed at 1 atm. Zinc (BP 1185 K) has the highest vapour pressure in this region and is present in greater quantity than sodium because more was included in the calculation, the fact that sodium has the lower boiling point as an element (BP 1156 K) is not directly relevant. In the case of lithium and magnesium, their vapour pressures are determined by equilibrium with the oxidised species, including the spinel, and the ruling oxygen partial pressure. The partial pressures of Li and Na are therefore constant throughout region 2 with most of the Li and Mg forming more spinel. The partial pressure of lithium (BP 1600 K) turns out to be next in magnitude although it has a higher elemental boiling point than magnesium (BP 1376) and much more magnesium was added. The partial pressures of the monatomic metal vapours, diatomic nitrogen and oxygen, and NO are illustrated in Figs 2(b)–5(b).

As would be expected, if the amount of zinc used in the calculation is reduced the number of moles in the gas phase is reduced by the same amount and the partial pressure of zinc also falls. In contrast, if the amount of magnesium is reduced, the partial pressure of magnesium remains constant through region 2 and does not fall. This is because of the continuing equilibrium involving gaseous magnesium, the magnesium spinel and gaseous oxygen at virtually fixed partial pressure—the latter being determined by the equilibrium between aluminium nitride, alumina and gaseous nitrogen.

Region 3 essentially corresponds to an excess of oxygen being present, $\alpha = 0.91$ (corresponding to the point at which there is sufficient oxygen for complete oxidation of the aluminium in the system). Thus there is a rapid rise in oxygen partial pressure in this region. Aluminium nitride is absent from the system, the lithium and magnesium spinels

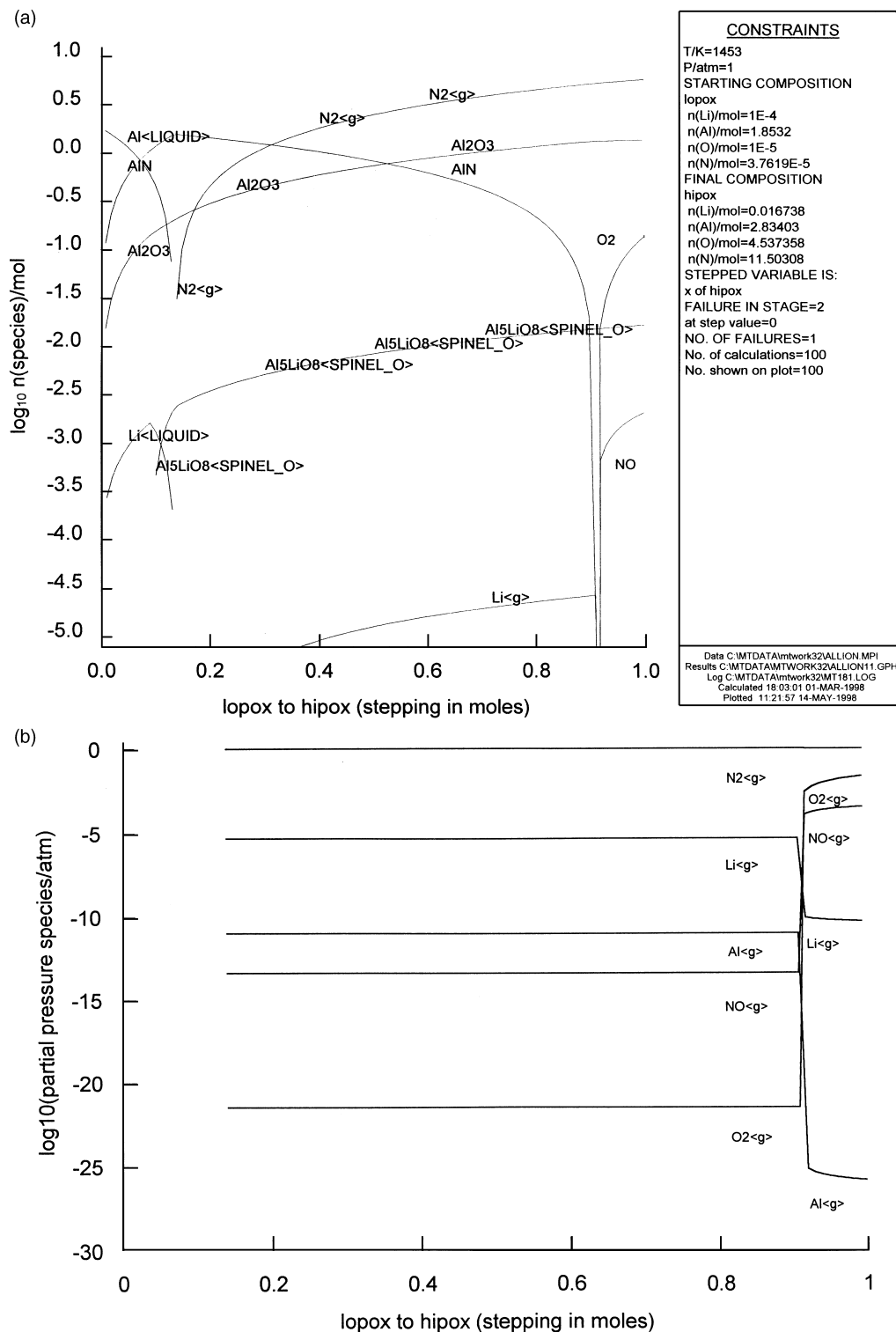


Fig. 2. (a) Condensed phases and (b) gas phases at 1453 K for Li doped directed melt oxidation into a preform body.

persist and β -alumina and the zinc spinel appear. The aluminium partial pressure now drops to a very low value.

3 Discussion

As indicated above directed melt oxidation is not an equilibrium process and thus some caution must be exercised in modelling it with equilibrium thermodynamics as such calculations do not deal with

any kinetic effects. For example, such calculations ignore phenomena such as wetting behaviour which would influence bulk motion during growth and the resultant distribution of reactants and products at the end of the reaction sequence. Detailed understanding of the reaction process therefore requires an interpretation of the results of the thermodynamic calculations in the light of those results obtained experimentally.

We have previously reported³⁻⁵ that reaction products in these systems contain alumina, a mixed

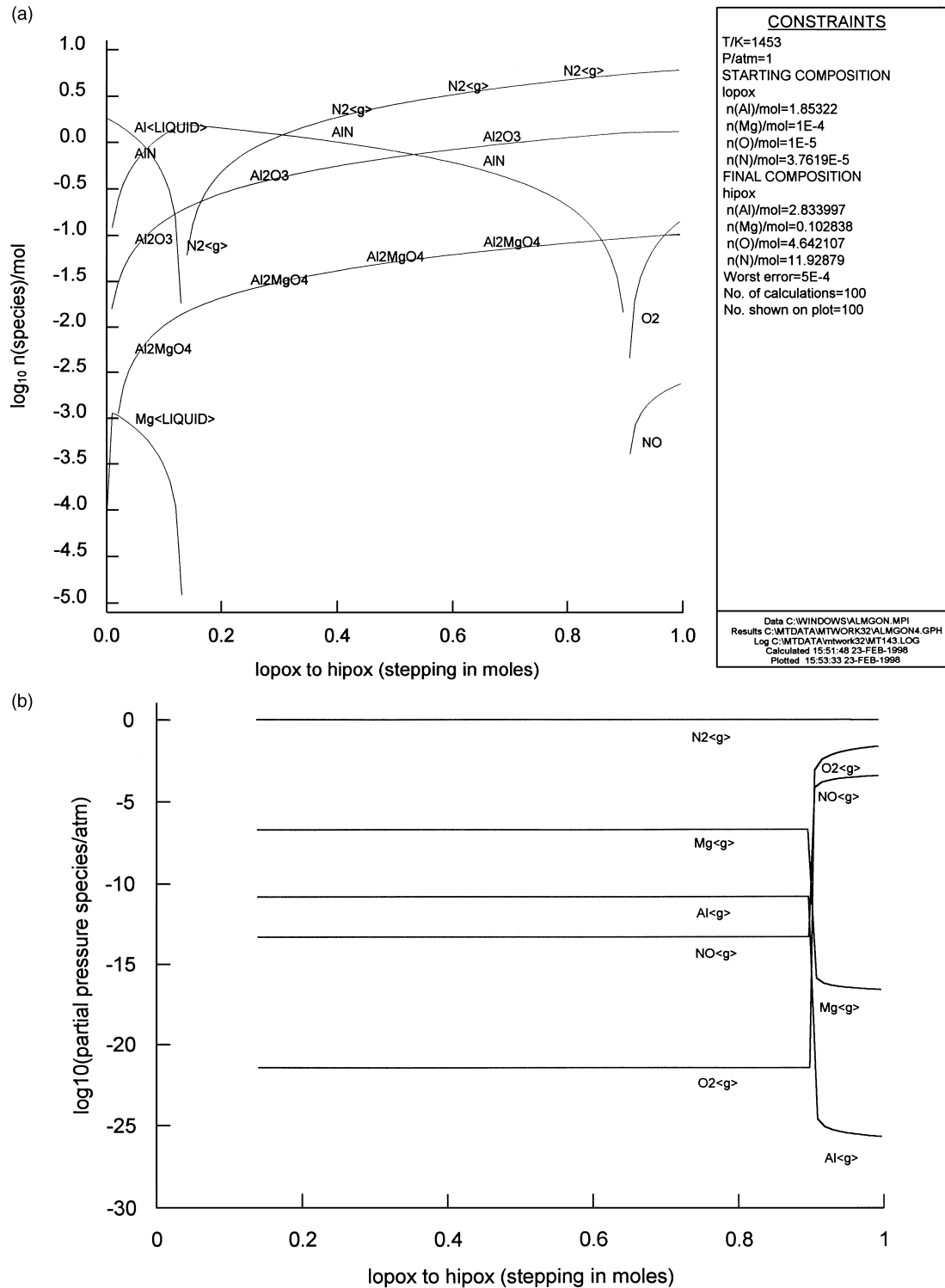


Fig. 3. (a) Condensed phases and (b) gas phases at 1453 K for Mg doped directed melt oxidation into a preform body.

oxide spinel phase and on occasion a small amount of aluminium nitride. The aluminium nitride always exists in isolated pockets within the bulk of the sample; from the calculations it is clearly seen that if there is any excess oxygen present during the reaction process then any aluminium nitride would tend to be oxidised to alumina. Therefore it is reasonable to conclude that aluminium nitride only remains after the reaction process has been completed in regions where oxygen ingress has been limited.

The thermodynamic calculations indicate that Mg and Li might be expected to lead to similar oxidation behaviour. Equally Na and Zn might be expected to lead to another type of oxidation behaviour. In addition there are some similarities between all four of these dopants elements, most obviously that they all lead to directed melt oxidation of Al. However the observed rates of oxidation and the detailed characteristics of the reaction product obtained with each dopant does vary.

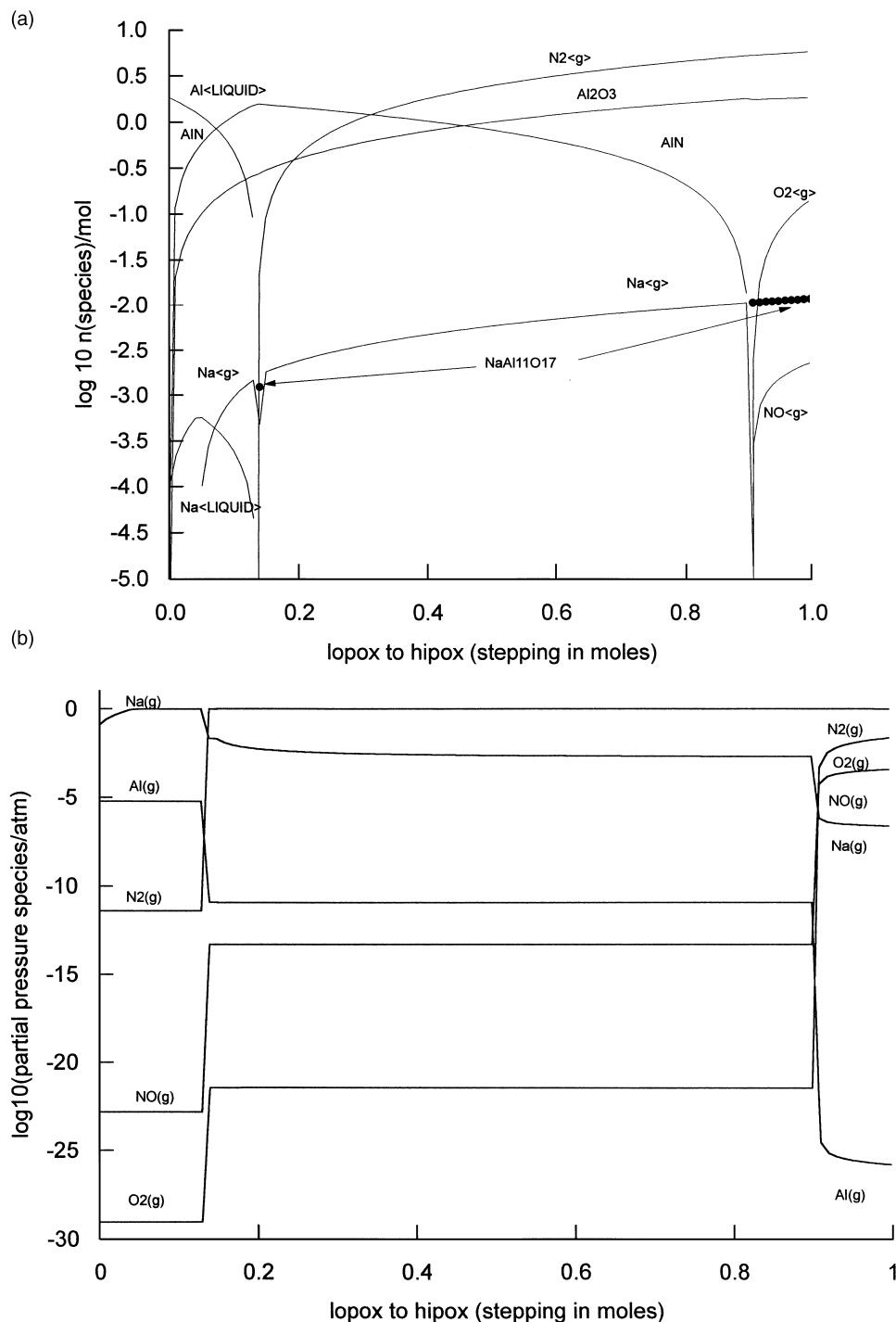


Fig. 4. (a) Condensed phases and (b) gas phases at 1453 K for Na doped directed melt oxidation into a preform body.

The highest dopant partial pressures for sodium are seen in region 1. Within a growing composite the region nearest the metal reservoir corresponds to the low α values and as the free surface is approached α increases. The greater dopant partial pressures at low α values mean that the volatile dopant will tend to move from regions of low α to regions with higher α values. This movement of dopant is believed to be crucial in maintaining the growth process. It can be seen from Figs 2(b)–5(b) that the partial pressures of Na and Zn are significantly higher than that of either Li or Mg in region 2. The high partial pressures of Zn and Na

in this region mean that it is more likely that Zn and Na will move further than either Li or Mg. Experimental data indicates that for systems involving a preform the Na doped system⁴ oxidises more rapidly than the Mg doped system³ which in turn oxidises more rapidly than the Li doped system.¹⁴ In fact the high partial pressure of Na generated in the Na doped system means that a preform has to be present for a reasonable, albeit porous, product to be produced. Without a preform Na vapour can travel significant distances and is deposited on the crucible walls distant from the reaction front resulting in a cessation of

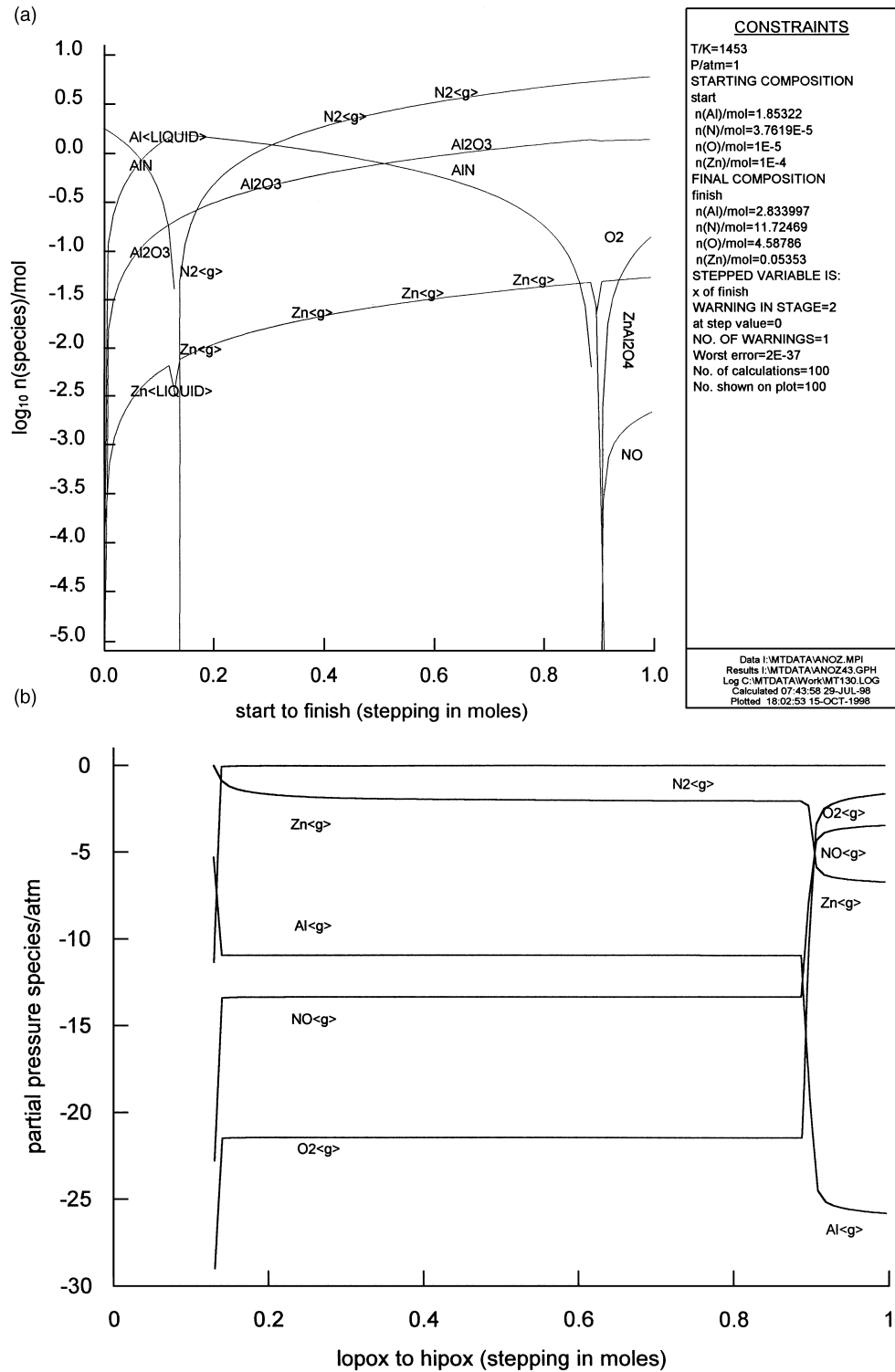


Fig. 5. (a) Condensed phases and (b) gas phases at 1453 K for Zn doped directed melt oxidation into a preform body.

growth.^{15,16} Other workers have similarly noted that zinc containing phases are deposited in regions away from the growing composite in the Zn doped system.¹⁷ Again this is in line with the thermodynamic predictions which indicate that Zn is highly volatile under the reaction conditions.

Mixed oxide phases are believed to be important in helping break down the initial stable alumina layer on the surface of aluminium. This layer would otherwise prevent bulk oxidation of the metal. Although with Na at 1453 K the mixed

oxide phase is not present across region 2, for all of the dopants the mixed oxide phase is present when there is an excess of oxygen (region 3). A mixed oxide layer is therefore expected at the outer surface of the reaction product; such layers have been seen experimentally.³⁻⁵ For Mg and Li the mixed oxide phase first appears in region 1 just before the elimination of the liquid aluminium alloy and therefore the stable alumina layer would be modified even if the oxygen supply was limited as is the case with growth into a preform body. The situation

is more complicated with Na but even here there is a small range of α values in region 2 where the mixed oxide phase exists and thus breakdown of the alumina layer can be envisaged under low oxygen conditions. However, there is no evidence of the zinc spinel in calculations made for region 1 of the Zn doped composites. The indication that zinc spinel does not form under low oxygen conditions, may help explain why some authors have reported that Zn on its own is insufficient to initiate directed melt oxidation growth.¹⁸ It should be noted however that other workers have not reported the same difficulties.¹⁷ Ongoing work in this laboratory indicates that it is easier to initiate growth with Zii when a preform is not present. With a preform the oxygen supply will be more limited and thus formation of the spinel phase may well be prevented thereby preventing oxidation growth.

Implicit in the above discussion is the idea that the reaction front proceeds at a uniform rate away from the initial melt surface. Experimentally the reaction front would often appear to be less uniform than this. For example at the preform/barrier powder boundary the growth is usually enhanced. It is likely that this is because air (oxygen) can move relatively easily down this boundary (there is no physical or chemical bond between the barrier powder and the preform) thus ensuring that the oxygen potential is quite high. Thus growth rates will be modified by local inhomogeneities in the initial preform body as well as by any inhomogeneities, such as splits, that might be generated during the reaction process. Although such features complicate the growth pattern, the basic features of the thermodynamic modelling are thought to still apply to individual regions of growth, with features such as splits effectively modifying the observed local rates of reaction rather than the detailed reaction process.

As mentioned above, phenomena such as wetting are also of importance during directed melt oxidation. Thermodynamic modelling does not give any direct indication of the extent of wetting within any of the systems. Thus although general conclusions about some of the necessary characteristics of dopants can be drawn such characteristics are not necessarily sufficient for the promotion of directed melt oxidation.

4 Conclusions

To maintain directed melt oxidation reactions dopants have to be volatile at the reaction temperature. The thermodynamic calculations indicate that the observed differences between the efficacies of the dopants studied arise from differences in the

partial pressures of the dopants at the reaction temperature. Although there is some variation in the aluminium and oxygen partial pressure with dopant species this variation is small compared to the variation in dopant partial pressure. Although a degree of dopant volatility is required experimental results indicate that if it is too elevated then the dopant may be readily lost to the reaction system which can result in a cessation of growth. Dopant loss is reduced by using systems containing preforms which restrict the rate at which the dopant is transported away from the main reaction front. Mg and Li are less volatile at the reaction temperatures and are therefore not readily lost from the reaction system.

The growth rate is not necessarily uniform across the whole sample. Instead it is effected by the presence of features such as fissures which can alter the rate of oxygen ingress to the reaction front. The oxygen gradients may therefore vary in quite a complicated fashion through the sample leading to uneven product growth. Uneven product growth also results when the dopants are too volatile at the reaction temperature.

Overall all of the dopants are not only volatile at the reaction temperature but they also produce mixed oxide phases with aluminium. These phases are required to help break down an otherwise stable alumina layer. Therefore potential dopants for directed melt oxidation of aluminium should both have elevated partial pressures at the proposed reaction temperature and should be capable of forming mixed oxide phases with aluminium.

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